# PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY $(\mbox{\sc pct})$

(51) International Patent Classification <sup>6</sup> :		(11) International Publication Number: WO 99/18330
E21D 9/06, C09K 7/08	A1	(43) International Publication Date: 15 April 1999 (15.04.99)
(21) International Application Number: PCT/EP (22) International Filing Date: 15 September 1998 (		(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT,
(30) Priority Data: 9720846.6 2 October 1997 (02.10.97) (71) Applicant (for all designated States except US): MB ING AG [CHCH]; Vulkaustrasse 110, CH-80- (CH), (72) Inventor; and (75) Inventor/Applicant (for US only): ELLENBERGI [CH/CH]; Rebbergstrasse 97, CH-8706 Feldmelle	ΓHOLI 18 Zūri ER, Pe	ch ter
(54) Title: FOAMING COMPOSITION		
stratum at the cutting face of an aqueous material comprisi	ng: (a)	a shield tunnelling apparatus, the process comprising the injection into the from 0.005-0.05 % by weight of a polyethylene oxide of weight-averages % by weight of a sulphate-containing anionic surfactant. The method is

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxenibourg	SN	Schegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbailan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	With	Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benio	IE	Ircland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL.	Israel	MR	Mauritania	UG	Uzanda
BY	Belarus	IS	Iceland	MW	Malawi	us	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE.	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL.	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand	ZW	Zunnanwe
CM	Cameroon	Kr	Republic of Korea				
CN	China	KR		PL PT	Poland		
CU		KZ	Republic of Korea Kazakstan		Portugal		
	Cuba			RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

FOAMING COMPOSITION

5 This invention relates to tunnel boring and to compositions for use therein.

Shield tunnel boring machines are increasingly used in the boring of tunnels, because they offer many advantages such as the ability to bore in a wide variety of strata. A shield boring machine comprises a circular rotatable cutting head mounted on a cylindrical

shield of similar diameter such that its axis of rotation coincides with the longitudinal axis of the shield. Within the shield there are contained means for feeding materials to the cutting head and means for conveying away the soil. Such machines perform well when the strata through which a tunnel is being bored is relatively hard and firm, but they do not perform so well in soft and crumbly strata which can make soil removal very difficult.

One way of seeking to overcome this problem is to apply a consolidation agent to the soil with the cutting head. This stabilises the coil allowing boring to be more accillus effected.

15 One way of seeking to overcome this problem is to apply a consolidation agent to the soi via the cutting head. This stabilises the soil, allowing boring to be more easily effected and the soil to be more easily removed.

Known stabilising agents have included bentonite slurrys and polymer suspensions. These

20 can lead to problems in certain soils, largely because they increase the soil water content
appreciably. Some soils (such as clays) can become sticky and difficult to remove and
clog up the cutting head, resulting in a substantial loss in efficiency. In a more recent
development, polymer foams have been suggested. These have the advantage that
considerably less fluid is placed in the soil per given volume. A typical foam formulation

25 will comprise a foaming agent and a foam stabilising agent, the latter generally a
surfactant. Thus, in operation, the foam is injected from ports in the cutting head into the
face being bored.

It has now been found that a particular foaming material gives especially efficaceous
results. The invention therefore provides a method of boring a tunnel through a stratum by
means of a shield tunnelling apparatus, the process comprising the injection into the
stratum at the cutting face of an aqueous material comprising

2

(a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular weight from 2,000,000 to 8,000,000; and

(b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

5

The invention additionally provides a foaming material adapted to assist the conveyance of soil from the cutting face of a shield tunneling apparatus, comprising

- (a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular
   weight from 2,000,000 to 8,000,000; and
  - (b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

Polyethylene oxides (PEO) are well-known items of commerce and a suitable material
may be selected from the wide range available. Typical examples are the "Polyox" (trade
mark) materials of Union Carbide. The anionic surfactant may be selected from any such
sulphate-containing surfactant known to the art. A particularly preferred type is
polyoxyalkylene alkyl ether sulphate, where the polyalkyleneoxide chain has an average
chain length of 2-3 alkylene oxide units. Typical commercial materials include the
"Alscope" (trade mark) series of Toho Chemical Industry Co.

Preferably the quantities of PEO and surfactant present are from 0.02 to 0.04% and from 0.15 to 0.4% by weight, respectively. Most preferably, the PEO quantity is from 0.03-0.04%.

25

The rest of the aqueous material is generally water, but other art-recognised ingredients (such as biocides and complexing agents) can be added in art-recognised quantities. In a preferred embodiment of the invention, the aqueous material additionally comprises urea, to the extent of from 0.03-0.8%, preferably 0.06-0.25% by weight. The invention

30 therefore also provides a tunnelling foaming additive consisting essentially of polyethylene oxide, sulphate-containing anionic surfactant and urea and water. Another especially useful ingredient is a foam improver. Foam improvers are materials which are well known in the art for their ability to stabilise foams. They are typically amines with long fatty acid chains derived from natural fats and oils, for example coconut 5 oil.

The aqueous material may be prepared and stored in advance as a single material, but it is preferred to provide it as two components which are mixed prior to use. In this case, one component comprises PEO and surfactant, and the other is a dilute aqueous solution of 10 PEO, typically at a weight concentration of from 0.007-0.015%, preferably from 0.015-0.06%. Both of course contain sufficient water to ensure that they are sufficiently fluid, and sufficient of the essential ingredients to give on mixing proportions of the size listed hereinabove - appropriate mixtures with respect to molecular weights and proportions are readily determined. The water content of the aqueous material should be such that it has a 15 viscosity as measured by the Bohlin System 3 apparatus, using spindle 1 of from 600-1200 mPa.s., and in the case of the two component embodiment, the water contents of the individual components should be such as to achieve this. The two-component embodiment is exceptionally storage-stable.

- 20 In operation, the aqueous material is supplied to the machine, where it is diluted to typically a 3% solution of total aqueous material in water and foamed by conventional means and injected into the tunnel face via ports in the cutting head. In addition, foam can also be injected from ports in the shield to strengthen the tunnel walls.
- 25 The invention is further described with reference to the following non-limiting worked examples.

## Example 1

The following materials are blended

5		parts by weight
	polyoxyalkylene alkyl ether sulphate $^{\mathrm{1}}$	8.58
	urea	5.00
	polyethylene oxide 2	1.20
	biocide <sup>3</sup>	0.02
10	complexing agent 4	0.02
	water	85.18

<sup>1 &</sup>quot;Alscope" W 140

This composition provides a concentrate for use, which use is demonstrated in Example 2.

## 20 Example 2

Testing of the composition of Example 1 on a soil.

The soil which is used is taken from Madrid where the tunnelling for the new metro has been especially difficult. The experiment consists of taking four 1000g-sized samples of this soil (a heavy clay), adding a material to three of these in an attempt to make it removable, agitating the mixture in a Hobart mixer for 3 minutes and then checking the viscosity by means of a Haake VT02 Viscometer. The stickiness of the material in the Hobart mixing bowl is also assessed.

<sup>2 &</sup>quot;Polyox" (trade mark) WSR-301

<sup>15 3 &</sup>quot;Biotack" (trade mark)

<sup>4 &</sup>quot;Clewat" (trade mark)

PCT/EP98/05905 5

To each of three 1000g samples are added one of the following:

- (a) 65g water
- (b) 65g of a 3% solution of a foaming agent "Rheocell" (trade mark), foamed 1:10 with air (1 volume solution to 9 volumes air)
- 5 (c) 65g of a 3% solution of the composition of Example 1 foamed 1:10 with air

In addition to the viscosity (which is an indication of the ease of soil removal from a cutting head), the stickiness of the material is assessed comparatively when cleaning out the mixing bowls. The ratings for stickiness are

10

15

- 1 very sticky, soil will not pour from bowl and is removable only with difficulty
- 2 sticky, soil will not pour from bowl, but can be removed relatively easily
- 3 not sticky, most soil pours out of bowl and the little residue remaining is easily removed.

The results are as follows:

		Viscosity (poise)	Stickiness
	mud alone	1000 <sup>1</sup>	1
20	(a) mud and water	300 ¹	1
	(b) mud and foaming agent	50 <sup>2</sup>	2
	(c) mud and Example 1	50 <sup>2</sup>	3
	composition		

25 <sup>1</sup> The measurements are made using a No. 2 spindle, used for thick liquids and paste.

It can be seen that the composition according to the invention gives substantial 30 improvements in both viscosity and stickiness, even though a bigger spindle (which normally gives a higher viscosity reading than a smaller one) was used.

<sup>&</sup>lt;sup>2</sup> A larger spindle (No.1) is used for thinner liquids and pastes.

6

## Example 3

## Example of a two-component system

5

A two-part system is formed by using 1 part of the composition of Example 1 with up to 10 parts of water which contain 1% by weight of "Polyox" WSR-301. The proportion of this polyethylene oxide solution is adjusted, depending on the water content of the mud involved.

10

When tested according to the procedure of Example 2, the composition gives the same excellent results as that of the composition of Example 1.

## Examples 4-7

15

A number of compositions according to the invention are prepared and tested according to the procedure set out in Example 2.

The compositions are shown in the following table:

20

Example No.	sulphate-	polyethylene	complexing	foam improver
	containing	<u>oxide</u>	agent	
	surfactant			
4	Zetesol NL2	Polyox	Cublen	Urea
		WSR-301	K2523	

7

5	Sulfetal	Polyox	Masquol	Aromox
	Cjot 60	WSRN-60K	P430 NA	MCD-W
6	Hostaspur OS-1	"	Sequion 50K33	Quiminox QL
7	Empicol	Polyox	Cublen	Aromox
	LX 42	WSR-301	AP1	C/12-W

The materials used are as follows:

5 "Zetesol" (trade mark) NL2 (ex Zschimmer & Schwarz) - sodium lauryl ether sulphate.

"Sulfetal" (trade mark) Cjot 60 (ex Zschimmer & Schwarz) monoisopropanolammonium lauryl sulphate.

10 "Hostaspur" (trade mark) OS-1 (ex Clariant) - sodium oleyl sulphonate.

"Empicol" (trade mark) LX 42 (ex Albright & Wilson) - sodium lauryl sulphate.

"Polyox" (trade mark) WSRN-60K (ex Union Carbide) - polyethylenexide, molecular 15 weight (weight-average) about 2 million.

"Polyox" WSR-301 - polyethylene oxide, molecular weight (weight-average) about 4 million.

20 "Cublen" (trade mark) K2523 (ex Zschimmer & Schwarz) - tripotassium hydroxyethane diphosphonic acid.

8

"Masquol" (trade mark) P 430 Na (ex Protex) - hexasodium ethylenediamine tetra(methylenephosphonic) acid.

"Sequion" (trade mark) 50 K 33 (ex Bozzetto) - hexapotassium ethylenediamine tetra(methylenephosphonic) acid.

"Aromox" (trade mark) C/12-W (ex Akzo-Nobel) - coco-bis-(2-hydroxyethyl) amine oxide.

10 "Aromox" MCD-W - cocodimethylamine oxide.

"Quiminox" (trade mark) QL (ex Qimidroga) cocodimethylamine oxide.

The test results obtained are rated 3, as are those of the compositions of Examples 15 1 and 3.

9

## Claims:

- A method of boring a tunnel through a stratum by means of a shield tunnelling apparatus, the process comprising the injection into the stratum at the cutting face of an aqueous material comprising
  - (a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average molecular weight from 2,000,000 to 8,000,000
- 10 (b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.
  - A method according to claim 1, wherein the sulphate-containing anionic surfactant
    is a polyoxyalkylene alkyl ether sulphate, where the polyalkyleneoxide chain has
    an average chain length of 2-3 alkylene oxide units.

15

5

- A method according to claim 1, wherein the quantities of polyethylene oxide and surfactant present in the aqueous material are from 0.02-0.04% and from 0.15-0.4% by weight, respectively.
- A method according to any one of claims 1-3, wherein the aqueous material additionally comprises urea.
  - A method according to any one of claims 1-3, wherein the aqueous material additionally comprises a foam booster.

25

- A foaming material adapted to assist the conveyance of soil from the cutting face
  of a shield tunnelling apparatus, comprising
- (a) from 0.005-0.05% by weight of a polyethylene oxide of weight-average
   molecular weight from 2,000,000 to 8,000,000
  - (b) from 0.05-0.5% by weight of a sulphate-containing anionic surfactant.

### INTERNATIONAL SEARCH REPORT

ional Application No PCT/FP 98/05905

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21D9/06 C09k C09K7/08

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 E21D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ·	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	W0 90 00187 A (J.PIERCE) 11 January 1990 see page 4, line 13 - line 30 see page 7, line 4 - page 9, line 14 see page 10, line 19 - page 11, line 2 see claims 1-4	1-6
Y	US 4 247 405 A (D.R. WIER) 27 January 1981 see column 2, line 42 - column 3, line 60; claims 1-7; example II	1-6
Y	US 3 215 200 A (W.H.KIRKPATRICK) 2 November 1965 see column 2, line 22 - column 3, line 23 see column 5, line 42 - line 73; claims 1,2	1-6
A	FR 2 690 709 A (SEPPIC) 5 November 1993 see claims 1-	1-6
1	,	

## Special categories of cited documents:

- Patent family members are listed in annex
- X Further documents are listed in the continuation of box C.
- A' document defining the general state of the lart which is not considered to be of particular rele 'E' earlier document but published on or atter the international
- filing date "L" document which may throw doubts on pnonty\_claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified).
- O' document reterring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "8" document member of the same natent familia Date of mailing of the international search report

Date of the actual completion of the international search

3 February 1999 10/02/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijewijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Boulon, A

Authorized officer

Form PCT/ISA/210 (second sheet) (July 1992)

1

## INTERNATIONAL SEARCH REPORT

Int tional Application No PCT/FP 98/05905

0.10		
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category <sup>1</sup>	Citation of document with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 098 (C-221), 9 May 1984 & JP 59 015476 A (SUMITOMO KAGAKU KOGYO KK), 26 January 1984 see abstract	1-6

## INTERNATIONAL SEARCH REPORT

information on patent family members

Inte onal Application No PCT/EP 98/05905

	itent document in search repor	t	Publication date		atent family member(s)		Publication date
WO	9000187	А	11-01-1990	US AU AU US	4959164 609689 3705789 519640	) B	25-09-1990 02-05-1991 04-01-1990 23-03-1993
US	4247405	A	27-01-1981	NONE			
US	3215200	A	02-11-1965	NONE			
FR	2690709	А	05-11-1993	AT AU DE DE DK EP ES WO GR NO	14274 426339: 6930469: 6930469: 63813: 063813: 209230: 932253: 302118: 94405:	B A L D L T 7 T 7 A 7 T B A 1 T	15-09-1996 29-11-1993 17-10-1996 13-02-1997 30-09-1996 15-02-1995 16-11-1993 31-12-1996 27-12-1994